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Project Summary

A Field Screening Method for Polychlorinated Biphenyl Compounds in Water

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The U.S. Environmental Protection Agency (EPA) has been exploring the complexation of silver ions with certain organic pollutants as part of a search for alternative low-cost, rapid field screening methods. The effort has resulted in a rapid, easy, and inexpensive procedure for determining polychlorinated biphenyls (PCBs) in water.

Based on previous testing of samples by General Electric Corporate Research and Development, a cosponsor of this project, there was a special interest in developing a field-screening procedure of PCB aqueous extracts performed from a current soil remediation procedure in which the extractant contained 1–3% surfactant by weight to enhance solubility of PCBs. A test was developed, based on forming complexes of PCBs with silver ions, which was followed by ultraviolet (UV) irradiation to yield metallic silver. The appearance of a gray-to-brown color, depending on PCB concentration, was used to signal the presence of PCBs. This method allows the test color to be directly compared with color charts to estimate the PCB concentration without the need for instrumentation. In addition to soil remediation monitoring, potential applications include well monitoring, wellhead protection monitoring, post-closure monitoring, and rapid laboratory screening.

For soil remediation monitoring, it was found that several varieties of filter paper or solid phase extraction (SPE) membranes could be used in a dipstick mode, followed by spraying with methanolic silver nitrate solution and irradiation with 254 nm light from a hand-held UV lamp to provide a color spot test. The detection range was 1–500 ppm in the presence of either 3% Renex KB™* or Neodol (R) 1-7™, surfactants currently being examined in soil remediation.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The overall challenge of field screening involves dealing with numerous pollutants within many classes (organic, inorganic, biomarker, and radionuclide), across various media, and in complex mixtures. The detection limits of field methods are not always as low nor as reliable and accurate as laboratory methods. However, the data quality objectives in a particular scenario may allow field methods to be used. For example, less accurate methods can be used to screen environmental samples prior to confirmatory laboratory analyses. A cost advantage results by reducing the number of required laboratory analyses.

Field screening methods may provide rapid performance at low cost to allow determination of whether a parameter of interest is present or absent, above or

* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

below a predetermined threshold at a given site, or at a concentration within a predetermined range of interest. Field screening methods can also be used in the field to identify the nature and extent of contamination at individual sites. A few field screening methods are currently available and additional ones are being developed. The most mature methods are based on gas chromatography and X-ray fluorescence. One of the clear trends is to miniaturize. Methods that are still in various stages of development include the use of fiber optic sensors and chemical microsensors, such as piezoelectric quartz microbalances and surface acoustic wave probes. The technologies developed as field screening methods conform to the monitoring and measurement needs of many EPA programs.

The need for field screening of ground water relates to protecting public water supply wells and well fields, following remediation efforts, and post-closure monitoring of hazardous waste disposal sites, as examples. Ground water contains many natural constituents, with the various species and concentrations depending on factors such as the specific geochemical environment and the source of ground water. The major anions that are usually analyzed for general water quality include bicarbonate, chloride, nitrate, and sulfate. Other general indicators include electrical conductivity, temperature, pH, dissolved oxygen, biochemical oxygen demand, chemical oxygen demand, total organic carbon, oxidation-reduction potential, total suspended solids, total dissolved solids, and turbidity.

The present research, described in the full report (based on the Master of Science thesis of Shen Lin, first author of this project summary), describes the development of a new concept for field screening that emphasizes speed, ease of application, low cost, and *in situ* water monitoring for following PCB soil remediation.

The central idea brought forward in this research was to form silver complexes with PCBs directly in the environmental samples and to display their comparative concentration levels through rapid development of a gray-to-brown coloration of finely-divided silver on SPE or filter paper substrates using a brief UV irradiation or sunlight. In other words, this new process combines development of a photo-gray or photo-brown coloration on various substrates and relates the color or shading to a color chart produced from known silver concentrations, and therefore PCB levels, in the environmental sample.

Approach

A preliminary step was to devise a convenient method for extracting and concentrating PCBs from the aqueous environmental samples. This was followed by the development of a chemical reaction or molecular association effect that could provide a visual signal for the presence of PCBs.

While liquid-liquid extraction can be used to separate organic components from aqueous solutions, the process is slow, labor intensive, and requires large volumes of solvents. The latter creates another potential pollution problem. With rising waste disposal costs, laboratory technologists today are turning to the use of SPE membranes to adsorb and concentrate the organic compounds directly from the water sample, avoiding the need for organic solvents. Filtering the solution through a SPE disk concentrates the solute through adsorption on the silicate matrix. Their specific adsorbing power is generally sufficient to allow SPE material to be cut into small tabs and used in a "dipstick" mode with the water sample.

The SPE disk or tab, exposed to PCBs in solution, generally shows *no color change* (other than possibly some coloration from suspended matter in the sample). The early literature (1970s) of thin-layer chromatography provided insight into possible visualization agents for the adsorbed PCBs on the SPE disks or tabs: PCBs can be reacted with silver nitrate to yield silver-PCB complexes. These complexes are not stable and UV irradiation from sunlight or other source rapidly breaks down the silver-organic complex. Free silver, in finely divided form, appears on the substrate as a gray-to-brown coloration. Based on the literature references, the decision was made to exploit this reaction and optimize the performance to provide adaptation for environmental monitoring. It was also found in the early experiments that if the PCB concentration is high enough, preconcentration, using SPE techniques, is not necessary. Filter paper can be spotted with this test solution directly, or a filter paper tab can be dipped into the solution.

Experimental

Two test formats were chosen for sample collection. One used small tabs, cut from SPE material or filter paper, and exposure to the water samples in a "dipstick" manner for several minutes. In a second test format, test solution was placed dropwise directly on the SPE or filter paper tabs. Other test formats, such as filtering the test solutions through the SPE or filter paper disks, could have been used but at a loss of ease for use in the field. It was decided to place developmental emphasis on the dipstick test format because of its simplicity and retained effectiveness.

When PCBs contaminate soil, they raise a specific environmental challenge in that they become firmly bound to the soil matrix because of their high molecular weight and low water solubility.

However, the presence of surfactants may increase the solubility of PCBs in water. The use of surfactants such as Renex™ and Neodol (R) 1-7™ (both nonionic compounds) is being examined by others in PCB soil-washing and remediation processes.

The development of a PCB detection test in the presence of these surfactants would serve to provide a very useful monitoring scheme to follow the soil-washing procedure. Surfactants such as these increase the solubility of PCBs to the 500 ppm range. At high concentration levels, the use of SPE techniques would not seem necessary. However, experiments using SPE membranes to concentrate PCBs further were included to increase the applicability of the test to other field screening scenarios.

Test solutions of the PCBs were prepared in methanol and diluted with deionized water, either with or without surfactant. Control solutions also contained surfactants, if used in the tests.

The SPE tabs (1 x 1 cm) were conditioned by dipping into methanol just before use; this allowed them to be wet easily by the aqueous test solutions. Tabs were either suspended in the various PCB test solutions for 30 minutes or dipped and quickly removed. They were then sprayed with 0.059 M silver nitrate in methanol. Irradiation followed with a UV lamp (254 nm) for 1–3 minutes. The UV lamp was held 1.5 cm from the tabs. The development of color, relative to a control tab after 1 minute, signaled the presence of PCBs.

Filter paper tabs (1 x 1 cm) were dipped into the PCB test solution, removed, sprayed with 0.059 M silver nitrate in methanol, and exposed for 3 minutes in the same manner as above. For simplicity in field testing and to avoid the need for instrumental readings, Ameritone™ paint color chips were used as standards for defining the exact color and intensity. All results were based on at least duplicate runs, with some being taken in triplicate.

Results and Discussion

Tests with SPE membranes (1-hour passive immersion), followed by silver nitrate visualization, detected PCBs at the 0.5–1.0 ppm level in the absence of surfactant; at 22–24 hours there was no improvement, but shortening the exposure time to 30 minutes raised the detection level to 5 ppm. SPE membranes were also used to extract PCBs from aqueous solution containing surfactant by exposing the tabs for 30 minutes. The detection limit varied from 0.5–5 ppm, depending on the type of PCB.

Tests with filter paper tabs (Whatman 541™) involved dipping and immediate removal, spraying with silver nitrate solution, and irradiating with UV light. The PCB solutions contained either Renex KB™ or Neodol 1-7™ surfactants. The results show that PCBs can be readily detected on Whatman 541 filter paper in the presence of these surfactants. The colors differed somewhat from SPE tabs, depending on the PCB and surfactant type.

At the high PCB level of 500 ppm, the test colors were not gray but brown with a trace of gray. The control tabs showed very little color even though the solutions contained 3% surfactant.

It is also interesting to note that dipping the Whatman 541 filter paper tabs and quickly removing them is about as sensitive as the technique in which SPE tabs (in the presence of surfactant) were allowed to stand for 30 minutes. It is suggested that the surfactant may be competing with the PCBs for adsorption onto the SPE medium.

As for possible interferences, it was expected that chloride ions would interfere in the visualization reaction since silver chloride, which is extremely sensitive to light, would be formed. The sensitivity for chloride ion was found to be 1 ppm in the absence of surfactants; no color was observed with 0.5 ppm. Positive tests were found with PCBs at 0.5 ppm, but the higher sensitivity is understandable since equivalent chloride would be available from the PCBs. The colors matched closely those obtained using PCBs, i.e., very light gray at 1 ppm and brown at the highest concentrations, i.e., 1000 ppm chloride ion. The chloride ion interference could be eliminated by adding a few granules of anion exchange resin (AG 1-X2™), lightly agitating, and continuing with the test in the usual manner. Results remained negative up to 1000 ppm chloride ion.

Summary and Conclusions

The objective was to develop a simple, alternative, and inexpensive test procedure for field screening PCBs in water. There was a special interest to determine whether the test would work well in the presence of 1–3% surfactants in order to follow the progress of washing or remediation of soils contaminated with PCBs.

A visual test requiring no instruments was developed based on forming silver ion complexes of PCBs from silver nitrate, followed by brief UV irradiation to form finely divided silver metal. The latter appeared as a gray or brown coloration, depending on PCB concentration. The test color can be easily compared to standard color charts or paint chips to give an estimate of the PCB level. In addition to soil-remediation monitoring, potential applications include well monitoring, wellhead protection monitoring, post-closure monitoring, and rapid screening of laboratory samples.

A number of factors were found to affect the sensitivity of the visualization reaction, including choice of test matrix, nature of the surfactant, wavelength and intensity of the light, and presence of possible interferences. These are described in more detail in the full report.

As expected, chloride ion was found to interfere. The chloride sensitivity was found to be 1 ppm in the presence of surfactants. The colors closely matched those obtained using PCBs. However, the chloride ion interference was eliminated by adding a few granules of an anion exchange resin to the test solution.

The potential of exploiting the results for a PCB field screening test is judged to be high. The findings can be used as a basis to further improve the PCB detection test and to develop new field screening methods for other pollutants.

A promising area for further research is the use of a catalyst for the dechlorination of PCBs (and other organohalogen compounds) that do not photosensitize silver ion reduction.

Also, a detailed examination of the chemistry of photography, including color photography, may identify other opportunities for enhanced sensitivity and selectivity. The use of indicators presorbed onto SPE membranes, which can both extract and detect pollutants in either water or air, appears to be a promising area to explore.

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The complete report, entitled "A Field Screening Method for Polychlorinated Biphenyl Compounds in Water," (Order No. PB95-129078; Cost: $17.50, subject to change) will be available only from

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